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# Interactions of an Azobenzene-Functionalized Anionic Amphiphile with Cationic Amphiphiles in Aqueous Solution

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Interactions between the azobenzene-containing amphiphile methyl octyl orange (MOO) and *n*-alkyltrimethylammonium bromides ($C_n$TAB, $n = 1, 6, 8, 10, 12, 16$) in aqueous solution have been studied using UV−vis spectroscopy. Interactions occur at concentrations below the critical micelle concentrations of the individual cationic surfactants ($n = 8, 10, 12, 16$) as indicated by a ca. 80 nm blue shift of the main absorption band of MOO. In addition, aggregation of MOO with $C_6$TAB, which is a hydrotrope rather than a surfactant, was also observed. The critical aggregation concentration (cac) of MOO determined by surface tension experiments was 0.68 mM. The cac's of aqueous mixtures of $C_n$TAB and MOO (1:1) were considerably lower than those of the individual surfactants. The absorption spectrum of MOO at concentrations above the cac in the 1:1 mixtures was also blue shifted with respect to the absorption spectrum of MOO in aqueous solution. Vesicular aggregates formed in equimolar aqueous mixtures of $C_n$TAB and MOO were characterized by means of cryo- and negative staining transmission electron microscopy. Vesicles are small and range in diameter from 8 to 15 nm although some vesicles having a diameter between 30 and 80 nm were also observed. Vesicle size distributions were confirmed using dynamic light scattering. Vesicle sizes decreased upon increasing the chain mismatch, and ultimately, vesicles transformed into micelles. Micelles were also formed in a 1:1 aqueous mixture of $C_6$TAB and MOO.

## Introduction

Surfactants containing an azobenzene chromophoric unit in the alkyl chain self-assemble into a variety of aggregates in aqueous solution. Aggregate morphologies in aqueous solution include micelles[1] and different types of bilayer structures.[2−6] In such aggregates, strong association of the chromophores is often observed. This is reflected by a change in the absorption and, when present, fluorescence spectra of the chromophores. A blue shift[3−7] of the absorption maximum of the aromatic moiety can be assigned to parallel interaction modes of the chromophores. This type of aggregation is called H-aggregation. By contrast, a red-shifted absorption band is attributed to aggregation of the chromophores in a head-to-tail fashion (J-aggregates).[8]

Aqueous mixtures of azobenzene-labeled surfactants and oppositely charged surfactants form vesicles[9,10] analogous to the formation of vesicles from mixtures of cationic and anionic surfactants.[11] Vesicle formation is indicated by a blue shift of the absorption maximum of the azobenzene units reflecting interaction of the chromophores.[9] The formation and disruption of vesicles can be controlled by photochemical E→Z isomerization of the azo unit.[10] The vesicles are able to encapsulate water-soluble compounds that are released upon isomerization of the azobenzene unit.

Aggregation of surfactants and azo dyes in aqueous solution has been extensively investigated. Methyl orange (MO, Chart 1) has attracted much attention in this respect.[12−17] Strong interactions of cationic surfactants and MO occur at concentrations far below the critical micelle concentration (cmc) of the individual surfactants and are characterized by a ca. 80 nm blue shift of the main absorption band of the dye. Dye aggregation of the H-type has been suggested to account for the spectral changes.[12,16] Dilution of the dyes over micelles occurs upon increasing the surfactant concentration, and under these conditions, the spectrum of the dye shifts to that of the dye in an organic environment.

Dye aggregation has also been proposed to be responsible for the short-wavelength absorption band of MO in the presence of cationic polysoaps and polymers.[18] A hypsochromic shift in the absorption spectrum of dendrimers

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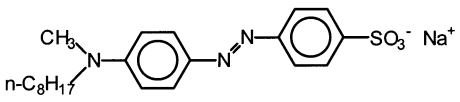
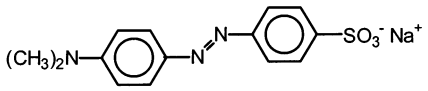
**Chart 1. Structures of Methyl Octyl Orange (MOO) and of Methyl Orange (MO)**



**MOO**



**MO**

derivatized with azobenzene moieties has also been ascribed to interactions between the chromophores.[19] Similarly, the hypsochromic shift of $\lambda_{max}$ upon aggregation of azobenzene-based surfactants has been attributed to aggregation of the chromophoric units.[20] Moreover, parallel orientation of azobenzene units in cast films of azobenzene-containing amphiphiles has been verified by X-ray diffraction experiments.[21] MO molecules in Langmuir−Blodgett films composed of cationic surfactants and MO are oriented in a more or less parallel fashion and show a blue shift of the $\pi \rightarrow \pi^*$ absorption band as well.[22]

In this study, we have investigated the interactions of the azobenzene-containing anionic amphiphile methyl octyl orange (MOO, Chart 1) with cationic *n*-alkyltrimethylammonium bromide amphiphiles ($C_n$TAB where *n* is the number of carbons in the alkyl chain) in aqueous solution. In addition, aggregation of short-chain $C_n$TABs ($n = 1, 6$) with MOO in aqueous solution was also examined. The chromophore of MOO is structurally similar to that of MO, but the $C_8$ alkyl tail imparts surfactant properties to MOO. It was anticipated that an increase in hydrophobicity of the dye might result in interactions of MOO with $C_n$TABs with shorter alkyl tails than in the case of MO. Aggregation was followed by UV−vis spectroscopy, and the types of aggregates formed in aqueous solution were characterized by cryo and negative staining transmission electron microscopy (TEM). Aggregate sizes were also determined using dynamic light scattering. Critical aggregation concentrations were determined using surface tension and conductivity experiments.

## Experimental Section

**General Remarks.** *N*-Methylaniline was purchased from Aldrich, *n*-octyl bromide and 1-butanol came from Acros, and sulfanilic acid dihydrate came from Merck. $C_1$TAB (Aldrich), $C_6$TAB (Fluka), $C_8$TAB (Acros), $C_{10}$TAB (Lancaster), $C_{12}$TAB (Sigma), and $C_{16}$TAB (Merck) were dried in vacuo before use. $C_1$TAB and $C_6$TAB were recrystallized from 80% MeOH and EtOH, respectively. Diethyl ether was distilled from $P_2O_5$, and water was distilled in an all-quartz distillation unit. $^1$H NMR and $^{13}$C NMR spectra were measured at 200 or 300 MHz on a Varian Gemini-200 or a Varian VXR-300 MHz spectrophotometer, respectively.

**UV−Vis Spectroscopy.** UV−vis absorption spectra were recorded on a Perkin-Elmer $\lambda$5 spectrophotometer equipped with a thermostated cell compartment.

**Surface Tension Measurements.** Critical aggregation concentrations (cac's) were measured using a TVT 1 Lauda drop tensiometer. The water used was doubly distilled.

**Differential Scanning Calorimetry (DSC).** The Krafft temperature of MOO was determined on a Perkin-Elmer DSC-7 apparatus, using sealed stainless steel pans. Measurements were performed with heating rates of 3 °C/min, and cooling rates varied from 3 to 10 °C/min.

**Transmission Electron Microscopy.** Negatively stained electron micrographs were obtained using a JEM 1200 EX electron microscope operating at 80 kV. Samples were prepared on carbon-coated collodion grids and stained with uranyl acetate (UAc). Cryo electron microscopy was performed according to the following procedure: aliquots of surfactant solutions were deposited on holey carbon grids; the excess solution was blotted off using filter paper. The samples were vitrified by rapid plunging into liquid ethane. The grids were transferred to a Gatan model 626 cryo holder and examined at ca. −170 °C in a CM10 microscope (Philips) operating at 100 kV. Micrographs were recorded under low dose conditions.

**Dynamic Light Scattering.** Size distributions of vesicle solutions were determined at room temperature at a fixed angle of 90° with a Malvern Instruments Zeta Sizer 5000 using the Contin analysis mode. Measuring times were 400−500 s. Surfactant concentrations were between 5 and 10 mM.

***N*-Methyl-*N*-octylaniline.**[23] A mixture of 5.35 g (0.05 mol) of freshly distilled *N*-methylaniline, 9.65 g (0.05 mol) of *n*-octyl bromide, 6.9 g (0.05 mol) of potassium carbonate, and 50 mg (0.3 mmol) of potassium iodide in 100 mL of 99% *n*-butanol was stirred at 110 °C for 22 h. The reaction was performed under a nitrogen atmosphere. The mixture was allowed to cool to room temperature and filtered, and *n*-butanol was removed in vacuo. The residue was dissolved in 100 mL of diethyl ether, extracted with water, and dried over sodium sulfate. After removal of diethyl ether, the product was purified by vacuum distillation. Subsequently, column chromatography ($Al_2O_3$ act. III neutral) was performed using *n*-hexane as the eluent. *N*-Methyl-*N*-octylaniline was obtained as a colorless oil in 49% yield (5.37 g, 24.5 mmol). $^1$H NMR (300 MHz, $CD_3OD$): $\delta$ 0.85 (t, 3H, $CH_3$), 1.25 (m, 10H, $CH_2$), 1.52 (m, 2H, $CH_2$), 2.88 (d, 3H, $CH_3$), 3.25 (t, 2H, $CH_2$), 6.62 (m, 3H, ar), 7.18 (m, 2H, ar).

**4-[4-(*N*-Methyl-*N*-octylamino)phenylazo]benzenesulfonic Acid, Sodium Salt (Methyl Octyl Orange).** The formation of methyl octyl orange from *N*-methyl-*N*-octylaniline and sulfanilic acid was performed according to the synthesis of methyl orange.[24] $^1$H NMR (300 MHz, $CD_3OD$): $\delta$ 0.85 (t, 3H, $CH_3$), 1.32 (m, 10H, $CH_2$), 1.62 (m, 2H, $CH_2$), 3.30 (d, 3H, $CH_3$), 3.46 (t, 2H, $CH_2$), 6.80 (d, 2H, ar), 7.82 (m, 4H, ar), 7.92 (d, 2H, ar). $^{13}$C NMR (200 MHz, $CD_3OD$): $\delta$ 13.98 (p), 22.10, 26.39, 28.74, 28.91, 31.25 (s), 38.23 (p), 51.59 (s), 111.3, 121.2, 125.0, 126.6 (t), 142.3, 148.8, 151.6, 152.2 (q). Anal. Calcd $C_{21}H_{28}N_3SO_3Na$ (425.52): C, 59.28; H, 6.63; N, 9.87; S, 7.53; Na, 5.40. Found: C, 59.25; H, 6.78; N, 9.80; S, 7.63; Na, 5.35.

## Results and Discussion

**Aggregation Behavior of MOO.** MOO is only slightly soluble in aqueous solution at room temperature, but the solubility shows a dramatic increase at the Krafft temperature[25] of 44.1 °C as determined by differential scanning calorimetry.

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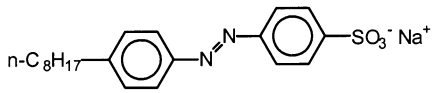
**Chart 2. Structure of Sodium 4-(4′-Octylphenylazo)benzenesulfonate**




The cmc of MOO as determined by surface tension experiments at 46 °C equals 0.68 mM. This concentration is slightly larger than that of sodium 4-(4′-octylphenylazo)-benzenesulfonate (Chart 2), which has a cmc of 0.43 mM.[1] The difference is attributed to the presence of the relatively polar nitrogen atom at the 4-position that connects the alkyl group to the azobenzene part in MOO. Apparently, this effect is larger than the effect of increased hydrophobicity of the alkyl part of MOO due to the additional $CH_3$ substituent. The cross-sectional headgroup area of MOO at the air−water interface ($a_s$)[26] calculated from the Gibbs adsorption isotherm[27] is 87 Å$^2$. Also, this area is larger than that for sodium 4-(4′-octylphenylazo)benzenesulfonate ($a_s$ = 76.0 Å$^2$) indicating a decreased packing efficiency of MOO at the air−water interface compared to that of sodium 4-(4′-octylphenylazo)benzenesulfonate. This conclusion is supported by surface tensions at the cmc ($\gamma_{cmc}$) of both compounds: 40.1 mN m$^{-1}$ for sodium 4-(4′-octylphenylazo)benzenesulfonate and 49.8 mN m$^{-1}$ for MOO. Although the $C_{12}$ analogue of MOO is claimed to form vesicles in aqueous solution,[2] MOO is thought to form micelles since no electron microscopic evidence for vesicle formation was obtained. Moreover, the structurally similar sodium 4-(4′-octylphenylazo)benzenesulfonate forms micelles when dispersed in water.[1]

**UV−Vis Spectroscopy.** MOO is a micropolarity reporter molecule since its long-wavelength absorption band is sensitive to medium effects. In water, the wavelength of maximum absorption ($\lambda_{max}$) of MOO is positioned at 472 nm, whereas it is situated at 431 and 427 nm in methanol and ethanol, respectively. Azo dyes are often used to report the presence of surfactant aggregates in aqueous solution.[28] When binding to surfactant assemblies occurs, a shift of the absorption maximum of the dye is observed.

Interactions have been studied of $C_n$TABs with MOO in aqueous solution using UV−vis spectroscopy. In these experiments, the MOO concentration was kept constant at 25 $\mu$M, whereas the $C_n$TAB concentration was varied. Measurements were performed with an excess of cationic amphiphile. The MOO concentration in UV−vis experiments is well below its cmc of 0.68 mM as determined by drop tensiometry. Figure 1 shows the effect of different concentrations of $C_{16}$TAB on the absorption spectrum of MOO. The intensity of the 472 nm absorption band characteristic for MOO in aqueous solution decreases upon addition of small amounts of $C_{16}$TAB. Further addition of surfactant produces a new band with a maximum at ca. 392 nm. This band is replaced by a band with a maximum around 415 nm at higher surfactant concentrations; the latter band is characteristic for MOO bound to cationic micelles. The new band around 392 nm appearing in the absorption spectrum of MOO at surfactant concentrations smaller than the cmc is analogous to the short-wavelength absorption band as observed previously in studies of the interactions of cationic amphiphiles with MO, EO, and pMR.[13−17]

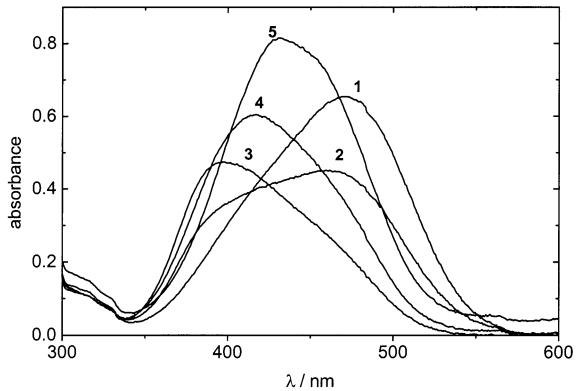



**Figure 1.** Effect of $C_{16}$TAB on the absorption spectrum of MOO. [$C_{16}$TAB] (M): (1) 0, (2) 5 × 10$^{-6}$, (3) 5 × 10$^{-5}$, (4) 0.23 × 10$^{-3}$, (5) 4.5 × 10$^{-3}$. [MOO] = 25 $\mu$M; $T$ = 30 °C.

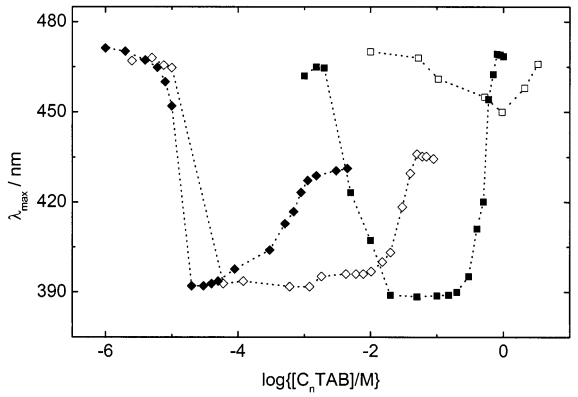



**Figure 2.** Effect of $C_n$TAB on the position of the absorption maximum of MOO: (◆) $C_{16}$TAB, (◇) $C_{10}$TAB, (■) $C_6$TAB, (□) $C_1$TAB. [MOO] = 25 $\mu$M; $T$ = 30 °C.

Interactions of MOO and $C_n$TABs having shorter alkyl tails than $C_{16}$TAB have also been investigated using absorption spectroscopy. Figure 2 shows the effects of $C_n$TAB ($n$ = 1, 6, 10, 16) on the wavelength of maximum absorption of MOO. For clarity, data for $C_8$TAB and $C_{12}$TAB are not shown, but these surfactants have an effect on the absorption spectrum of MOO similar to that observed for other $C_n$TABs. All $C_n$TABs ($n \geq 6$) interact with MOO at low $C_n$TAB concentration as reflected by the appearance of the short-wavelength absorption band. Upon increasing the $C_n$TAB concentration, the short-wavelength absorption band gradually disappears and the position of the wavelength of maximum absorption shifts to longer wavelengths. Aggregation of MO and cationic surfactants having alkyl tails shorter than 12 carbon atoms does not occur at a MO concentration of 25 $\mu$M.[16] The fact that the short-wavelength absorption band is observed in the absorption spectrum of MOO at 25 $\mu$M upon addition of short-chain $C_n$TABs ($n \geq 6$) confirms the importance of hydrophobic interactions in the aggregation process.

Wavelengths of maximum absorption of MOO at low (concentration < cmc) and at high cationic surfactant concentrations (concentration > cmc) are shown in Table 1. In the case of $C_6$TAB and $C_1$TAB, these numbers correspond to the plateau values of $\lambda_{max}$ at low and at high

(25) The Krafft temperature is the temperature where the cmc equals the solubility of the surfactant. See for example: Van Doren, H. A. In *Carbohydrates as Organic Raw Materials III*; Van Bekkum, H., Roper, H., Vorhagen, F., Eds; VCH Publishers: Weinheim, Germany, 1996; p 255.

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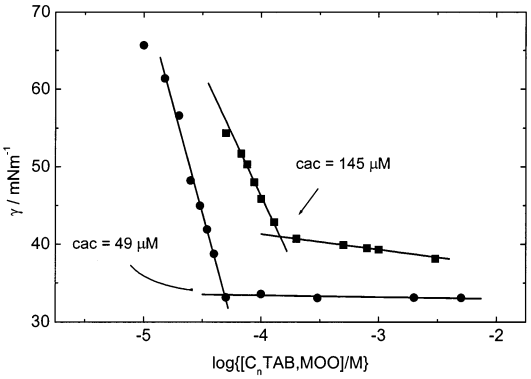


**Figure 3.** Surface tension plots of 1:1 aqueous mixtures of $C_{10}$TAB and MOO (●) and of $C_6$TAB and MOO (■). $T = 30$ °C.

**Table 1. Position of the Absorption Maximum of MOO in Aqueous Solutions of $C_n$TAB at Low and at High $C_n$TAB Concentrations**

| *n* | $\lambda_{MOO}$/nm (low $C_n$TAB concentration) | $\lambda_{MOO}$/nm (high $C_n$TAB concentration) |
|---|---|---|
| 1 | 450 | 466 |
| 6 | 392 | 469 |
| 8 | 395 | 446 |
| 10 | 392 | 435 |
| 12 | 393 | 430 |
| 16 | 392 | 431 |

$C_n$TAB concentration (Figure 2). The absorption maximum at high surfactant concentrations shifts to longer wavelengths upon decreasing *n*. This indicates that the polarity of the microenvironment of MOO in $C_n$TAB aggregates increases with a decrease in *n*.

The short-wavelength absorption band is at 394 ± 2 nm for $C_6$TAB to $C_{16}$TAB. Although $C_6$TAB is a hydrotrope rather than a surfactant molecule, it does show indications of aggregation above a concentration of 0.5 *m*[29] most likely forming loosely packed structures with small aggregation numbers in aqueous solution.[30] The present results indicate that MOO sits in a relatively aqueous environment in these aggregates confirming the open structures of such assemblies.

The wavelength for maximum absorption of MOO in the presence of 1 M $C_1$TAB is positioned at ca. 450 nm. Apparently, surfactant-induced reduction of electrostatic interactions between ionic headgroups of MOO by $C_1$TAB is sufficient to induce aggregation of MOO. However, the relatively small decrease of $\lambda_{max}$ suggests that aggregation is not as efficient as in the case of $C_n$TABs with longer alkyl tails. This explanation is confirmed by the fact that inorganic salts such as sodium bromide and ammonium bromide also induce the short-wavelength absorption band in the spectrum of MOO.

**Aggregation Behavior of Mixtures of *n*-Alkyltrimethylammonium Bromides and MOO: Surface Tension Experiments.** The cac's of equimolar aqueous mixtures of $C_n$TAB ($n = 6, 8, 10$) and MOO were determined by drop tensiometry. Figure 3 shows surface tension plots for equimolar mixtures of (a) $C_{10}$TAB and MOO and (b) $C_6$TAB and MOO. The cac of a 1:1 aqueous mixture of $C_6$TAB and MOO is 145 $\mu$M; that for $C_{10}$TAB and MOO is 49 $\mu$M. The cac's of mixtures are dramatically lower than those of the individual components. For example, the cac of $C_{10}$TAB is 60.2 mM[31] and that of MOO

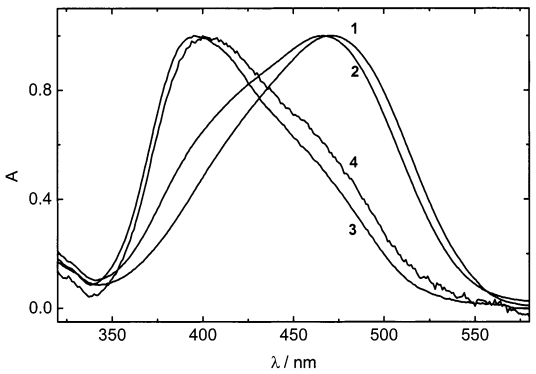


**Figure 4.** Normalized absorption spectra of MOO in an aqueous solution of $C_{10}$TAB (1:1) at surfactant concentrations below and above the cac. [$C_{10}$TAB] = [MOO]/$\mu$M: (1) 0, (2) 20, (3) 50, (4) 500.

is 0.68 mM. A dramatic lowering of the cac in a mixture of cationic and anionic surfactants is commonly observed and is mainly caused by the favorable Gibbs energy as a result of electrostatic attraction of the oppositely charged headgroups of the surfactant molecules.[32] A lowered surface tension of the mixture compared to that of the individual surfactants could be explained by an increased surface activity of the electroneutral catanionic surfactant.[33−35] The cac of a 1:1 aqueous mixture of $C_8$TAB and MOO is 81 $\mu$M (plot not shown).

A plot of the logarithm of the cac against the number of carbon atoms in the $C_n$TAB alkyl tail shows an approximately linear increase upon increasing *n* although the number of data points (3) is small. Unfortunately, areas of the surfactants at the air−water interface cannot be exactly determined since the Gibbs adsorption isotherm[27] cannot be applied: the isotherm can be used only when dealing with 1:1 electrolytes or when excess salt is present. However, the slopes of surface tension plots before the cac's increase upon increasing *n*. Since the area of the surfactant at the air−water interface is proportional to the slope$^{-1}$,[27] this pattern indicates that the cross-sectional areas of surfactants at the air−water interface decrease upon increasing *n*.

Figure 4 shows normalized absorption spectra of MOO in an aqueous solution of $C_{10}$TAB (1:1) at surfactant concentrations below (curves 1 and 2) and above (curves 3 and 4) the cac (49 $\mu$M). Clearly, absorption spectra of MOO are blue shifted at concentrations above the cac compared to those below the cac. The position of the blue-shifted absorption band is similar to that at low (25 $\mu$M) MOO concentrations. Also in this case, dye aggregation is held responsible for the short-wavelength absorption band. *N*-Decyltrimethylammonium−methyl orange ($C_{10}$TA−MO) forms vesicles at a concentration of 0.84 mM. Also in this case, the absorption spectrum of the dye showed a blue shift when aggregates were formed.[16]

**TEM Study of the Aggregation Behavior of Mixtures of $C_n$TAB and MOO.** Aggregates formed in aqueous solutions of MOO and $C_n$TAB ($n = 1, 6, 8, 10, 12, 16$) were characterized with TEM using cryo and negative staining techniques. Cryo TEM was performed to visualize aggregates formed from 1:1 aqueous mixtures of $C_n$TAB ($n = 6, 8, 10$) and MOO.

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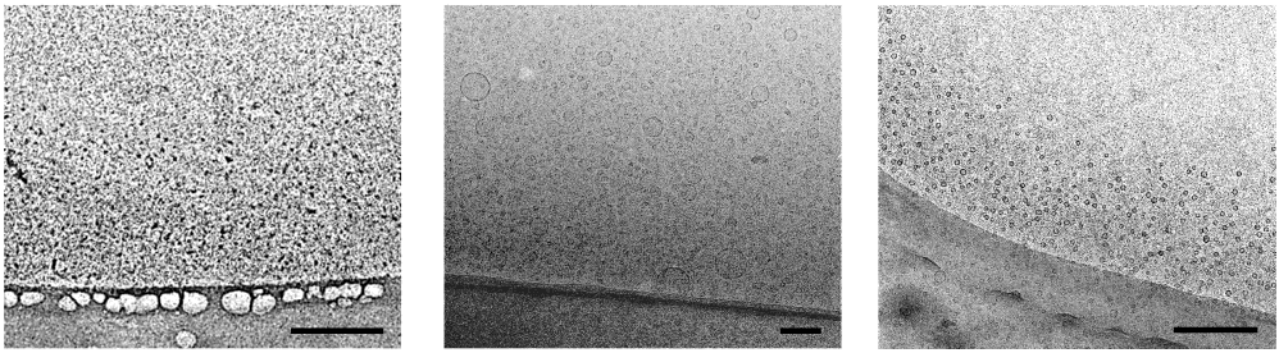

**Figure 5.** Cryo electron micrographs of micelles formed in an aqueous mixture of 5 mM $C_6$TAB and 5 mM MOO (left), vesicles formed in an aqueous mixture of 9 mM $C_8$TAB and 9 mM MOO (center), and vesicles formed in an aqueous mixture of 9 mM $C_{10}$TAB and 9 mM MOO (right). Each bar represents 100 nm.

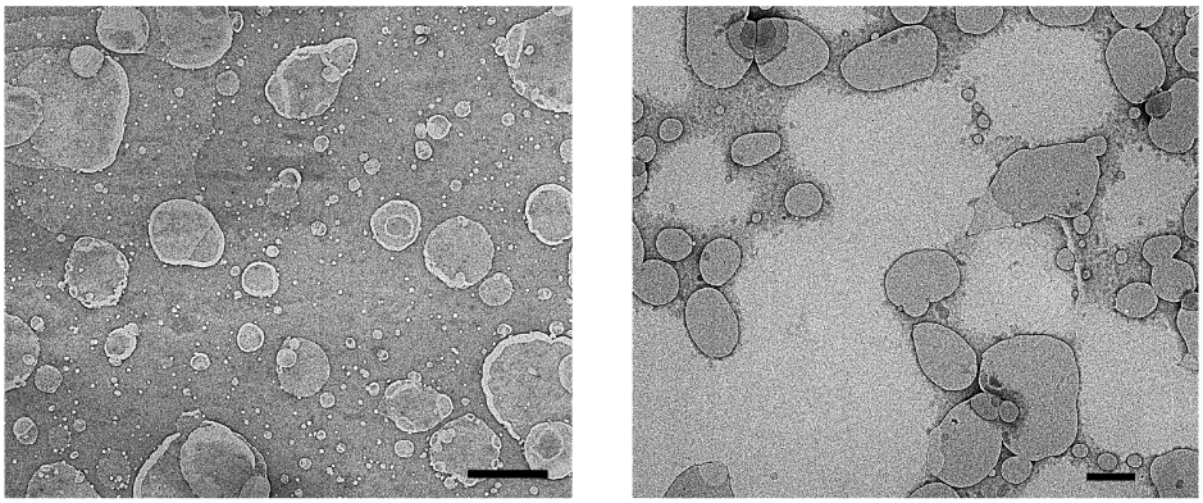

**Figure 6.** Negative staining electron micrographs of vesicles formed in an aqueous mixture of 2 mM $C_{12}$TAB and 2 mM MOO (left) and vesicles formed in an aqueous mixture of 1 mM $C_{16}$TAB and 1 mM MOO (right). The bar represents 500 nm.

Spheroidal micelles were observed in aqueous solutions of $C_6$TAB and MOO, whereas aqueous solutions of $C_8$TAB and MOO and aqueous mixtures of $C_{10}$TAB and MOO displayed vesicle formation. The vesicles are small: the average diameter estimated from cryo TEM pictures is 8−12 nm. We suggest that the stability of these small vesicles benefits from the charge compensation which reduces headgroup repulsion and from interdigitation of the alkyl chains. Some larger vesicles ranging in diameter from 20 to 70 nm have been observed, although their number density is much smaller. Figure 5 shows cryo electron micrographs of aggregates formed in equimolar aqueous mixtures of $C_n$TAB ($n$ = 6, 8, 10) and MOO. Formation of vesicles in $C_n$TAB/MOO aqueous mixtures when $n \geq 8$ and formation of micelles in the mixtures for $n = 6$ are consistent with the increase in area of surfactants at the air−water interface as observed in surface tension experiments.

Equimolar aqueous mixtures of $C_n$TAB ($n$ = 8, 10, 12, 16, 18) and MOO are found to form vesicles ranging in diameter from 25 nm to 1 $\mu$m as observed by negative staining TEM. Similar to cryo TEM experiments, small vesicles (10−20 nm) are also observed in aqueous mixtures of $C_8$TAB and MOO and of $C_{10}$TAB and MOO. In addition, large clumps are observed. Most likely, vesicles aggregate or fuse under the influence of the staining agent. Vesicles observed in 1:1 aqueous mixtures of $C_{12}$TAB, $C_{16}$TAB, and $C_{18}$TAB and MOO range in diameter from 25 to 200 nm. Large vesicles ranging in diameter from 400 to 700 nm are also observed. Figure 6 shows some examples.

**Table 2. Mean Vesicle Diameters as Determined by Dynamic Light Scattering**

| compound[a] | diameter/nm[b] |
|---|---|
| $C_8$TAB/MOO (5 mM) | 15.5 (4.7) |
| $C_{10}$TAB/MOO (9 mM) | 12.9 (4.1) |
| $C_{12}$TAB/MOO (5 mM) | 24.6 (7.0) |
| $C_{16}$TAB/MOO (2.5 mM) | 59.0 (15.1) |
| $C_{18}$TAB/MOO (0.5 mM) | 84.1 (29.3) |

[a] Surfactant concentrations are given in parentheses. [b] Peak width at half-height in parentheses.

Size distributions of vesicles formed from $C_n$TAB and MOO in aqueous solution studied by dynamic light scattering (DLS) are presented in Table 2. Surfactant concentrations are between 0.5 and 10 mM; size distributions are determined 1−2 h after mixing of both components. The mean diameters of $C_n$TAB/MOO vesicles increase upon increasing the tail length of $C_n$TAB, which corresponds to a decrease in the mismatch of the lengths of the apolar parts of MOO and $C_n$TAB. The length of the apolar part of MOO is comparable to that of a $C_{16}$ chain. Table 3 shows tail lengths of $C_n$TAB as estimated from Tanford's equation[36] and the length of the apolar part of MOO as indicated from geometry optimization by the ACD program package[37] using the ChemSketch LAB product.

Aqueous mixtures of cationic and anionic surfactants (or catanionic surfactants) usually form bilayer structures,

(36) Tanford, C. *J. Phys. Chem.* **1972**, *76*, 3020.
(37) ACD/ChemSketch Advance Chemistry Development/Inc. version 1.50, Toronto, Canada.

**Table 3. Lengths of Apolar Moieties of $C_n$TAB and MOO**

| compound | tail length/Å |
|---|---|
| $C_6$TAB | 9.1 |
| $C_8$TAB | 11.6 |
| $C_{10}$TAB | 14.2 |
| $C_{12}$TAB | 16.7 |
| $C_{16}$TAB | 21.7 |
| $C_{18}$TAB | 24.3 |
| MOO | 21.5[a] |

[a] Length of apolar moiety.

whereas micelles are formed by the separate surfactants.[11,34,35,38,39] Usually, these vesicle solutions crystallize after a few hours, although sometimes they are stable for a few days. The stability decreases upon increasing chain match and upon increasing surfactant concentration. Precipitation is commonly observed in mixtures of cationic and anionic surfactants especially when either the mixing ratio approaches 1:1 or the surfactant alkyl tails have equal lengths.[39] Since vesicles are generally formed upon the input of mechanical energy, the formation of vesicles from $C_n$TAB and MOO is an example of spontaneous vesicle formation.[11] However, the vesicles cannot be called equilibrium vesicles since the latter have to satisfy the following criteria: (1) they are unilamellar and formed upon dispersing dry surfactants in aqueous solution without the input of chemical or mechanical treatment (so they are formed spontaneously), (2) they do not aggregate with time, and (3) unilamellar vesicles are reformed when catanionic vesicles are disrupted by any physical or chemical treatment. Since $C_n$TAB/MOO vesicles crystallize upon aging, requirement 2 is not fulfilled.

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## Conclusions

The interactions of the anionic micelle-forming azo dye MOO and cationic $C_n$TAB surfactants have been studied using UV−vis spectroscopy. Aggregation of $C_n$TAB and MOO produces a new band in the absorption spectrum of MOO, which is ca. 80 nm blue shifted with respect to the absorption band of a single MOO molecule in aqueous solution. Interactions occur at concentrations below the cmc of the cationic surfactants and have been attributed to dye aggregation in a parallel fashion (H-aggregation).[8]

The critical aggregation concentration of MOO as determined by surface tension experiments is 0.68 mM. The aggregation behavior of equimolar aqueous mixtures of MOO and $C_n$TAB ($n$ = 6, 8, 10, 12, 16, 18) was studied using surface tension experiments and electron microscopy. The cac's of aqueous mixtures are dramatically lower than those of the individual surfactants. Moreover, vesicles are formed in aqueous mixtures of MOO and $C_n$TAB when $n \geq 8$ whereas micelles are formed in an equimolar aqueous mixture of $C_6$TAB and MOO. Vesicles formed in aqueous solutions of *n*-alkyltrimethylammonium bromides and MOO with different lengths of the alkyl tails are small with rather narrow size distributions. Vesicle sizes increase upon decreasing the alkyl tail asymmetry of $C_n$TAB and MOO.

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